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ON MOSELEY'S LAW FOR X-RAY SPECTRA

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While engaged in making interpolations, by the method of least squares, of unknown from known wave-lengths of high frequency spectra I noticed certain systematic deviations from Moseley's law which led me to investigate three interesting questions that have not been previously discussed, probably because the older data did not seem to be sufficiently accurate to justify close mathematical analysis. These questions are: (i) How accurately does Moseley's law reproduce the observed wave-lengths? (ii) What empirical formula will represent the numerical data within the limits of experimental error? and (iii) What is the order of magnitude of the high frequency radiations of elements having small atomic numbers and of which the spectra have not yet been obtained? In the following paragraphs definite answers will be given to questions (i) and (ii), while a tentative solution of the third problem is necessitated by the fact that it involves extrapolation. The wave-lengths used in the computations were taken from the recent papers by M. Siegbahn, W. Stenström, and E. Friman. These data were chosen because they are the latest, they were all obtained in the same laboratory with the same spectrometers, and they constitute the most extensive, accurate and consistent set available.

Moseley's law is that, for any one series (α, β, γ, etc.), the square-root of the frequency of the lines is a linear function of the atomic numbers of the radiating elements. In symbols $\sqrt{\nu_N} = a + b\,N$, where $\nu_N \equiv$ frequency, $N \equiv$ atomic number, a and b are constants for one series. When a and b are calculated by the method of least squares, from the 48 known wave-lengths of the L-α_1 series, extending from zinc ($N = 30$, $\lambda = 12.346$ A) to uranium ($N = 92$, $\lambda = 0.911$ A), the values

obtained lead to wave-lengths which show a systematic deviation from the experimental data. In other words, a 'smooth' curve can be drawn through the points having as abscissae the atomic numbers and as ordinates the corresponding percentages by which the calculated wave-lengths are algebraically greater than the experimental values. The extreme deviations are $+2.00\%$, -0.62%, and $+ 0.46\%$ for *Zn*, *Ce*, and *U*, respectively. Since the glancing angles are said to be correct within 0.3% it follows that the extreme interval of deviation (2.62%) must be real and that Moseley's law does not hold exactly over the entire range. In the case of the L-β_1 series for which 46 wave-lengths from arsenic ($N = 33$, $\lambda = 9.449$ A) to uranium ($\lambda = 0.720$ A) are given, another smooth curve of departure is obtained, the extreme deviations being $+13.35\%$, -3.06%, and $+ 5.84\%$, corresponding to *As*, *Nd*, and *U*, in the order named. The range 16.41% certainly cannot be accounted for as due only to experimental error. The data for the L-γ_1 series extend from zirconium ($N = 40$, $\lambda = 5.386$) to uranium ($\lambda = 0.615$) and comprise 36 wave-lengths. The deviations for the associated curve of departure are found to be $+9.22\%$, -1.68%, and $+3.96\%$ for *Zr*, *Yb*, and *U*, respectively. Unfortunately, only a portion of the literature relating to the K series is at present accessible to me. Nevertheless, the 20 wave-lengths of the means of the K-α_1 and K-α_2 series extending from sodium ($N = 11$, $\lambda = 11.951$ A) to germanium ($N = 32$, $\lambda = 1.259$ A), exhibit departures from the linear relation which are greater than the probable errors of the experimental numbers. In this case the original investigators state, and also give data to show, that the wave-lengths for the same line obtained from different negatives agree to within 1 or 2 tenths of one per cent. Just as for the L-series, so here, the curve of departure with respect to the linear law deviates more and more as the smallest atomic number is approached. The deviation for magnesium was found to be $+0.41\%$, and for sodium $+0.74\%$. The answer to the first question is, therefore, that Moseley's law does not hold for the entire range of the L-series and that it seems to be slightly inexact for the most intense lines of the K-series.

The second question proposed may be answered at once. The empirical equation

$$\sqrt{\nu_N} = A + B\,N + C\,(D + N)^{-1}$$

was found to represent the L-series well within the limits of experimental error even when the values of the parameters a', b', C, and D were obtained by graphical processes and not by the method of least squares.

This equation results from adding the correction function $a' + b' N + C (D + N)^{-1}$ to Moseley's formula. From the mathematical point of view the correction terms mean that the residuals (δ) of Moseley's law conform to the hyperbola $N\delta + c_1\delta + c_2 + c_3N + c_4N^2 = 0$, which differs from the general conic solely in the omission of the term that would involve the square of the residuals. In the case of the L-β_1 series—for which the linear law shows the greatest departures from the experimental data—the deviations of the more complicated formula were only + 0.15%, −0.13%, and + 0.23% for *As*, *Nd*, and *U*, respectively. In all cases examined B was positive while A, C, and D were negative. D was always an integer and, although the mathematical analysis does not preclude the possibility of fractional values, this peculiarity may be accidental and not may have physical significance.

Evidence in favor of the opinion that the wave-lengths of the K-series fall in the unexplored region between 600 A and 12 A will now be adduced. Substitution of unity for N in Moseley's formula leads to the *infra-red* wave-length 138.7μ, in the case of the mean K-α series. When the members of this formula are squared a parabolic equation *with related coefficients* is obtained. When N is replaced by 1 in the more general parabolic expression $\nu_N = a_0 + a_1N + a_2N^2$ it is found that $\lambda_1 = 366$ A. Under the same conditions the cubic $\nu_N = b_0 + b_1 N + b_2 N^2 + b_3 N^3$ gives $\lambda_1 = 130$ A. The last equation fits the known wave-lengths better than either of the preceding parabolic formulae, especially for the longest wave-lengths (smallest values of N). The probable error of one residual is $\pm$ 0.183% for Moseley's formula (squared) and $\pm$0.102% for the cubic, that is, nearly twice as good on the whole. Since the extrapolated wave-length becomes shorter as the equation is made to conform more closely to the experimental data and since the values obtained from the power expansions with independent coefficients are both less than 400A it seems plausible to conclude that the experimental wave-lengths when found will fall in the ultra-Lyman region. Extrapolation for the L-series would be premature for the reasons that the interval from $N = 30$ to $N = 1$ is too great and the law of nature is not yet known.

In conclusion, I desire to express the hope that the present paper, which is tentative and by no means final, may stimulate experimental research in the difficult but very important region of the spectrum lying between the shortest wave-length (600 A) published by Lyman and the longest determined by Friman.